

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
28 March 2002 (28.03.2002)

PCT

(10) International Publication Number
WO 02/24789 A2

(51) International Patent Classification⁷: **C08J 3/00**

(21) International Application Number: **PCT/US01/29724**

(22) International Filing Date:
21 September 2001 (21.09.2001)

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
60/234,150 21 September 2000 (21.09.2000) US
09/777,512 6 February 2001 (06.02.2001) US

(71) Applicant: **OUTLAST TECHNOLOGIES, INC.**
[US/US]; 6235 Lookout Road, Boulder, CO 80301 (US).

(72) Inventors: **MAGILL, Monte, C.**; 449 Westview Court,
Longmont, CO 80501 (US). **HARTMANN, Mark, H.**;
256 Rockview Drive, Superior, CO 80027 (US).

(74) Agents: **GALLIANI, William, S.**; Cooley Godward LLP,
3000 El Camino Real, Five Palo Alto Square, Palo Alto,
CA 94306-2155 et al. (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 02/24789 A2

(54) Title: **POLYMERIC COMPOSITES HAVING ENHANCED REVERSIBLE THERMAL PROPERTIES AND METHODS OF MANUFACTURING THEREOF**

(57) Abstract: A polymeric composite having enhanced reversible thermal properties is manufactured. A temperature regulating material is mixed with a dispersing polymeric material to form a first blend. The first blend is processed to form granules, and the granules are mixed with a matrix polymeric material to form a second blend. The second blend is processed to form the polymeric composite. The polymeric composite may be formed in a variety of shapes, such as, for example, pellets, fibers, flakes, sheets, films, rods, and so forth. The polymeric composite may be used as is or incorporated in various articles and applications where a thermal regulating property is desired. The polymeric composite may be further processed to form a variety of articles having enhanced reversible thermal properties, such as, for example, melt spun synthetic fibers.

POLYMERIC COMPOSITES HAVING ENHANCED REVERSIBLE THERMAL PROPERTIES AND METHODS OF MANUFACTURING THEREOF

FIELD OF THE INVENTION

5

The present invention relates to polymeric composites and their manufacture. More particularly, the present invention relates to polymeric composites comprising one or more temperature regulating materials that are useful in the manufacture of melt spun synthetic fibers.

10

BACKGROUND OF THE INVENTION

Many fabric materials are made from synthetic fibers. While the spirit and scope of this invention is not to be limited to the following definition, a fiber is typically considered to have a length several times (e.g., 100 times or more) greater than its diameter. Conventionally, two processes are used to manufacture synthetic fibers: a wet solution process and a melt spinning process. The wet solution process is generally used to form acrylic fibers, while the melt spinning process is generally used to form nylon fibers, polyester fibers, polypropylene fibers, and other similar type fibers. As is well known, a nylon fiber comprises a long-chain synthetic polyamide polymer characterized by the presence of an amide group -CONH-, a polyester fiber comprises a long-chain synthetic polymer having at least 85 percent by weight of an ester of a substituted aromatic carboxylic acid unit, and a polypropylene fiber comprises a long-chain synthetic crystalline polymer having at least 85 percent by weight of an olefin unit and typically having a molecular weight of about 40,000 or more.

The melt spinning process is of particular interest since a large portion of the synthetic fibers that are used in the textile industry are manufactured by this technique. The melt spinning process generally involves passing a melted polymeric material through a device that is known as a spinneret to thereby form a plurality of individual synthetic fibers. Once formed, the synthetic fibers may be collected into a strand or made into a cut staple. Synthetic fibers can be used to make woven or non-woven fabric materials, or alternatively, synthetic fibers can be wound into a yarn to be used thereafter in a weaving or a knitting process to form a synthetic fabric material.

Phase change materials have been incorporated into acrylic fibers to enable the fibers to provide enhanced reversible thermal properties and to enable fabric materials made from such fibers to perform similar functions. This is readily accomplished, in part due to the high levels of volatile materials (e.g., solvents) typically associated with the wet solution process of forming acrylic fibers. However, it is more problematic to incorporate phase change materials into melt spun synthetic fibers, since high levels of volatile materials are typically not present or desired in the melt spinning process. Previous attempts to incorporate phase change materials into melt spun synthetic fibers typically involved mixing the phase change materials with a standard fiber-grade thermoplastic polymer to form a blend and subsequently melt spinning this blend to form the synthetic fibers. Such attempts generally led to inadequate dispersion of the phase change materials within the fibers, poor fiber properties, and poor processability unless low concentrations of phase change materials were used. However, with low concentrations of the phase change materials, the desired enhanced reversible thermal properties normally associated with use of the phase change materials can be difficult to realize.

It is against this background that a need arose to develop polymeric composites comprising phase change materials that would be useful in the manufacture of melt spun synthetic fibers.

SUMMARY OF THE INVENTION

In one innovative aspect, the present invention relates to a method of manufacturing a polymeric composite, wherein the method comprises: (a) mixing a temperature regulating material with a dispersing polymeric material to form a first blend; (b) processing the first blend to form granules; (c) mixing the granules with a matrix polymeric material to form a second blend; and (d) processing the second blend to form the polymeric composite.

In another innovative aspect, the present invention relates to a method of manufacturing a polymeric composite useful to produce an article having enhanced reversible thermal properties, wherein the method comprises: (a) melting a dispersing polymeric material to form a first melt; (b) dispersing a temperature regulating material in the first melt to form a first blend, wherein the temperature regulating material comprises a phase change material; (c) processing the first blend to form granules; (d) melting a matrix polymeric material to form a second melt; (e) dispersing the granules in the second melt to

form a second blend; and (f) processing the second blend to form the polymeric composite.

5 In still another innovative aspect, the present invention relates to a method of manufacturing a polymeric composite, wherein the method comprises: (a) melting a dispersing polymeric material to form a first melt; (b) dispersing a temperature regulating material in the first melt to form a first blend, wherein the temperature regulating material comprises a phase change material; (c) mixing the first blend with a matrix polymeric material to form a second blend; and (d) processing the second blend to form the polymeric composite.

10 In yet another innovative aspect, the present invention relates to a method of manufacturing pellets useful to produce an article having enhanced reversible thermal properties, wherein the method comprises: (a) melting a dispersing polymeric material to form a first melt; (b) dispersing a plurality of microcapsules containing a phase change material in the first melt to form a first blend; (c) cooling the first blend to form a first solid;
15 (d) granulating the first solid to form granules; (e) melting a matrix polymeric material to form a second melt; (f) dispersing the granules in the second melt to form a second blend; (g) cooling the second blend to form a second solid; and (h) granulating the second solid to form the pellets.

20

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the nature and objects of the invention, reference should be made to the following detailed description taken in conjunction with the accompanying drawings, in which:

25 FIG. 1 illustrates a manufacturing process to form a polymeric composite in accordance with an embodiment of the invention;

FIG. 2 illustrates a manufacturing process to form a polymeric composite in accordance with another embodiment of the invention; and

30 FIG. 3 illustrates a manufacturing process to form a polymeric composite in accordance with a further embodiment of the invention.

DETAILED DESCRIPTION

The present invention relates to polymeric composites comprising one or more temperature regulating materials and methods of manufacturing the same. Polymeric composites in accordance with various embodiments of the invention have the ability to absorb or release thermal energy to reduce or eliminate heat flow. The polymeric
5 composites may exhibit, for example, improved dispersion or higher loading levels of a temperature regulating material. The polymeric composites may be formed in a variety of shapes, such as, by way of example and not by limitation, pellets, fibers, flakes, sheets, films, rods, and so forth. The polymeric composites may be used as is or incorporated in various articles and applications to provide a thermal regulating property while providing
10 improved strength to the articles and applications. For example, polymeric composites in accordance with various embodiments of the invention may be used in textiles (e.g., fabric materials), apparel (e.g., outdoor clothing, drysuits, and protective suits), footwear (e.g., socks, boots, and insoles), medical products (e.g., thermal blankets, therapeutic pads, incontinent pads, and hot/cold packs), containers and packagings (e.g., beverage and food
15 containers, food warmers, seat cushions, and circuit board laminates), buildings (e.g., insulation in walls or ceilings, wallpaper, curtain linings, pipe wraps, carpets, and tiles), appliances (e.g., insulation in house appliances), and other products (e.g., automotive lining material, sleeping bags, and bedding).

Polymeric composites in accordance with various embodiments of the invention
20 may be further processed to form a variety of articles having enhanced reversible thermal properties. For instance, an embodiment of the polymeric composite comprises pellets that are useful to form synthetic fibers, for injection molding processes, or for extrusion processes. Use of these pellets may provide benefits that are achieved by incorporating a temperature regulating material into the articles, which articles include, by way of example
25 and not by limitation, fibers such as nylon fibers, polyester fibers, polyethylene fibers, and polypropylene fibers, films, foams, and injection molded articles.

A polymeric composite according to some embodiments of the invention may comprise a temperature regulating material, a dispersing polymeric material, and a matrix polymeric material. According to some embodiments of the invention, the polymeric
30 composite is a solidified melt mixture of the temperature regulating material, the dispersing polymeric material, and the matrix polymeric material. Typically, the temperature regulating material is uniformly dispersed within the polymeric composite. The dispersing polymeric material and the matrix polymeric material may be the same or different.

Depending on the method of manufacturing the polymeric composite, desirability of further processing, or the particular application of the polymeric composite, the polymeric composite may comprise one or more additional components, such as, for example, water, surfactants, dispersants, anti-foam agents (e.g., silicone containing compounds and flourine
5 containing compounds), antioxidants (e.g., hindered phenols and phosphites), thermal stabilizers (e.g., phosphites, organophosphorous compounds, metal salts of organic carboxylic acids, and phenolic compounds), microwave absorbing additives (e.g., multifunctional primary alcohols, glycerine, and carbon), reinforcing-fibers (e.g., carbon
10 fibers, aramid fibers, and glass fibers), conductive fibers or particles (e.g., graphite or activated carbon fibers or particles), lubricants, process aids (e.g., metal salts of fatty acids, fatty acid esters, fatty acid ethers, fatty acid amides, sulfonamides, polysiloxanes, organophosphorous compounds, and phenolic polyethers), fire retardants (e.g., halogenated
compounds, phosphorous compounds, and boron compounds), and so forth.

According to some embodiments of the invention, the temperature regulating
15 material may comprise one or more phase change materials. In general, a phase change material may comprise any substance (or mixture of substances) that has the capability of absorbing or releasing thermal energy to reduce or eliminate heat flow at or within a temperature stabilizing range. The temperature stabilizing range may comprise a particular transition temperature or range of transition temperatures. A phase change material used in
20 conjunction with various embodiments of the invention may be capable of inhibiting a flow of thermal energy during a time when the phase change material is absorbing or releasing heat, typically as the phase change material undergoes a transition between two states (e.g., liquid and solid states, liquid and gaseous states, solid and gaseous states, or two solid states). This action is typically transient, e.g., may last until a latent heat of the phase
25 change material is absorbed or released during a heating or cooling process. Thermal energy may be stored or removed from the phase change material, and the phase change material typically can be effectively recharged by a source of heat or cold. By selecting an appropriate phase change material, the polymeric composite may be formed for any application thereof.

30 According to some embodiments of the invention, a phase change material may be a solid/solid phase change material. A solid/solid phase change material is a type of phase change material that typically undergoes a transition between two solid states (e.g., a crystalline or mesocrystalline phase transformation) and hence typically does not become a liquid during use.

Phase change materials that can be incorporated in polymeric composites in accordance with various embodiments of the invention include a variety of organic and inorganic substances. Exemplary phase change materials include, by way of example and not by limitation, hydrocarbons (e.g., straight chain alkanes or paraffinic hydrocarbons, 5 branched-chain alkanes, unsaturated hydrocarbons, halogenated hydrocarbons, and alicyclic hydrocarbons), hydrated salts (e.g., calcium chloride hexahydrate, calcium bromide hexahydrate, magnesium nitrate hexahydrate, lithium nitrate trihydrate, potassium fluoride tetrahydrate, ammonium alum, magnesium chloride hexahydrate, sodium carbonate decahydrate, disodium phosphate dodecahydrate, sodium sulfate decahydrate, and sodium 10 acetate trihydrate), waxes, oils, water, fatty acids, fatty acid esters, dibasic acids, dibasic esters, 1-halides, primary alcohols, aromatic compounds, clathrates, semi-clathrates, gas clathrates, anhydrides (e.g., stearic anhydride), ethylene carbonate, polyhydric alcohols (e.g., 2,2-dimethyl-1,3-propanediol, 2-hydroxymethyl-2-methyl-1,3-propanediol, ethylene glycol, polyethylene glycol, pentaerythritol, dipentaerythritol, pentaglycerine, tetramethylol 15 ethane, neopentyl glycol, tetramethylol propane, monoaminopentaerythritol, diaminopentaerythritol, and tris(hydroxymethyl)acetic acid), polymers (e.g., polyethylene, polyethylene glycol, polypropylene, polypropylene glycol, polytetramethylene glycol, and copolymers, such as polyacrylate or poly(meth)acrylate with alkyl hydrocarbon side chain or with polyethylene glycol side chain and copolymers comprising polyethylene, 20 polyethylene glycol, polypropylene, polypropylene glycol, or polytetramethylene glycol), metals, and mixtures thereof.

Table 1 provides a list of exemplary paraffinic hydrocarbons that may be used as the phase change material in the polymeric composites according to some embodiments of the invention.

Table 1

Paraffinic Hydrocarbon	No. of Carbon Atoms	Melting Point °C
n-Octacosane	28	61.4
n-Heptacosane	27	59.0
n-Hexacosane	26	56.4
n-Pentacosane	25	53.7
n-Tetracosane	24	50.9
n-Tricosane	23	47.6
n-Docosane	22	44.4
n-Heneicosane	21	40.5
n-Eicosane	20	36.8
n-Nonadecane	19	32.1
n-Octadecane	18	28.2
n-Heptadecane	17	22.0
n-Hexadecane	16	18.2
n-Pentadecane	15	10.0
n-Tetradecane	14	5.9
n-Tridecane	13	-5.5

A phase change material can be a mixture of two or more substances (e.g., two or more of the exemplary phase change materials discussed above). By selecting two or more different substances (e.g., two different paraffinic hydrocarbons) and forming a mixture thereof, a temperature stabilizing range can be adjusted over a wide range for any particular application of the polymeric composite. According to some embodiments of the invention, a phase change material may comprise a copolymer of two or more substances (e.g., two or more of the exemplary phase change materials discussed above).

According to some embodiments of the invention, the temperature regulating material may comprise a phase change material in a raw form (e.g., the phase change material is non-encapsulated at either a micro or macro level). During manufacture of the polymeric composite, the phase change material in the raw form may be provided as a solid

in a variety of forms (e.g., bulk form, powders, pellets, granules, flakes, and so forth) or as a liquid in a variety of forms (e.g., molten form, dissolved in a solvent, and so forth).

According to other embodiments of the invention, the temperature regulating material may further comprise a containment structure that encapsulates, contains, surrounds, or absorbs a phase change material. The containment structure may facilitate handling of the phase change material while offering a degree of protection to the phase change material from manufacturing conditions (e.g., high temperature or shear forces) associated with forming the polymeric composite or articles made from the polymeric composite. Moreover, the containment structure may serve to prevent leakage of the phase change material from the polymeric composite or from an article formed therefrom.

As an example of the containment structure, the temperature regulating material may comprise a plurality of microcapsules that contain the phase change material, which microcapsules are typically uniformly dispersed within the polymeric composite. The microcapsules may be formed as hollow shells enclosing the phase change material and may comprise individual microcapsules formed in a variety of regular or irregular shapes (e.g., spherical, ellipsoidal, and so forth) and sizes. The individual microcapsules may have the same or different shapes or sizes. According to some embodiments of the invention, the microcapsules may have a maximum linear dimension (e.g., diameter) ranging from about 0.01 to about 100 microns. In one presently preferred embodiment, the microcapsules will have a generally spherical shape and will have a maximum linear dimension (e.g., diameter) ranging from about 0.5 to about 3 microns. Other examples of the containment structure include, by way of example and not by limitation, silica particles (e.g., precipitated silica particles, fumed silica particles, and mixtures thereof), zeolite particles, carbon particles (e.g., graphite particles, activated carbon particles, and mixtures thereof), and absorbent materials (e.g., absorbent polymeric materials, superabsorbent materials, cellulosic materials, poly(meth)acrylate materials, metal salts of poly(meth)acrylate materials, and mixtures thereof). For instance, the temperature regulating material may comprise silica particles, zeolite particles, carbon particles, or an absorbent material impregnated with a phase change material.

The polymeric composite may comprise from about 5 percent to about 70 percent by weight of the temperature regulating material. According to some embodiments of the invention, the polymeric composite may comprise from about 10 percent to about 30 percent or from about 15 percent to about 25 percent by weight of the temperature regulating material. And, according to other embodiments, the polymeric composite may

comprise 15 percent by weight of the temperature regulating material. As further discussed below, some embodiments of the invention employ water-wetted microcapsules containing a phase change material to form the polymeric composite. In such embodiments, the polymeric composite may comprise an amount of water that is typically less than 1 percent by weight.

According to some embodiments of the invention, the polymeric composite may comprise two or more temperature regulating materials that differ from one another in some fashion. For instance, the two temperature regulating materials may comprise two different phase change materials or a phase change material in a raw form and a phase change material in an encapsulated form, respectively.

In general, the dispersing polymeric material may comprise any polymer (or mixture of polymers) that facilitates incorporating the temperature regulating material in the polymeric composite. According to some embodiments of the invention, the dispersing polymeric material may be compatible with or have an affinity for the temperature regulating material. Such affinity may facilitate dispersion of the temperature regulating material in an intermediate molten or liquid stage of the polymeric composite during its manufacture (e.g., in a melt of the dispersing polymeric material) and, thus, ultimately may facilitate incorporation of more uniform or greater amounts or loading level of a phase change material in the polymeric composite. In embodiments where the temperature regulating material further comprises a containment structure, the dispersing polymeric material may be selected for its affinity for the containment structure in conjunction with, or as an alternative to, its affinity for the phase change material. For instance, if the temperature regulating material comprises a plurality of microcapsules containing the phase change material, the dispersing polymeric material may be selected to have an affinity for the microcapsules (e.g., for a material or materials of which the microcapsules are formed). For instance, in some embodiments the dispersing polymeric material may be selected to comprise a polymer that is the same or similar to the polymer comprising the microcapsules (e.g., if the microcapsules comprise nylon shells, the dispersing polymeric material may be selected to comprise nylon). Such affinity may facilitate dispersion of the microcapsules containing the phase change material in an intermediate molten or liquid stage of the polymeric composite (e.g., in a melt of the dispersing polymeric material) and, thus, may ultimately facilitate incorporation of more uniform or greater amounts or loading level of the phase change material in the polymeric composite.

According to some embodiments of the invention, the dispersing polymeric material may have a slight or partial compatibility with or affinity for the temperature regulating material. Such partial affinity may be adequate to facilitate dispersion of the temperature regulating material and to facilitate processing at higher temperatures. At lower
5 temperatures and shear conditions and once the polymeric composite has been formed, this partial affinity may allow the temperature regulating material to separate out. For embodiments of the invention wherein a phase change material in a raw form is used, this partial affinity may lead to insolubilization of the phase change material and increased phase change material domain formation within the polymeric composite. According to
10 some embodiments of the invention, domain formation may lead to an improved thermal regulating property by facilitating transition of the phase change material between two states. For example, certain phase change materials such as paraffinic hydrocarbons may be compatible with polymeric materials comprising polyethylene or polyethylene-co-vinyl acetate at lower concentrations of the phase change materials or when the temperature is
15 above a critical solution temperature. Mixing of a paraffinic hydrocarbon and polyethylene or polyethylene-co-vinyl acetate may be achieved at higher temperatures and higher concentrations of the paraffinic hydrocarbon to produce a homogenous blend that may be easily controlled, pumped, and processed to form a polymeric composite. Once the polymeric composite has been formed and has cooled, the paraffinic hydrocarbon may
20 become insoluble and may separate out into distinct domains. These domains may allow for pure melting or crystallization of the paraffinic hydrocarbon for an improved thermal regulating property.

It should be recognized that the dispersing polymeric material may be selected to be compatible with or have an affinity for the matrix polymeric material. Here, the dispersing
25 polymeric material would serve as a compatibilizing link between the temperature regulating material and the matrix polymeric material to thereby facilitate incorporating the temperature regulating material in the polymeric composite.

Typically, the dispersing polymeric material will comprise a thermoplastic polymer (or a mixture of thermoplastic polymers) (i.e., one that can be heated to form a melt and
30 subsequently shaped or molded to form the polymeric composite). According to some embodiments of the invention, the dispersing polymeric material desirably comprises one or more low molecular weight polymers. A low molecular weight polymer typically has a low viscosity when heated to form a melt, which low viscosity may facilitate dispersion of the temperature regulating material in the melt. As one of ordinary skill in the art will

understand some polymers may be provided in a variety of forms having different molecular weights, since the molecular weight of a polymer may be determined by conditions used for manufacturing the polymer. Accordingly, as used herein, the term "low molecular weight polymer" may refer to a low molecular weight form of a polymer (e.g., a low molecular weight form of an exemplary polymer discussed below), and the term "molecular weight" may refer to a number average molecular weight, weight average molecular weight, or melt index of the polymer. For instance, a polyethylene having a number average molecular weight of about 20,000 (or less) may be used as the low molecular weight polymer in an embodiment of the invention. It should be recognized that a molecular weight or range of molecular weights associated with a low molecular weight polymer may depend on the particular polymer selected (e.g., polyethylene) or on the method or equipment used to mix the temperature regulating material with the low molecular weight polymer.

The dispersing polymeric material may comprise a polymer (or mixture of polymers) having a variety of chain structures that include one or more types of monomer units. In particular, the dispersing polymeric material may comprise a linear polymer, a branched polymer (e.g., star branched polymer, comb branched polymer, or dendritic branched polymer), or a mixture thereof. The dispersing polymeric material may comprise a homopolymer, a copolymer (e.g., statistical copolymer, random copolymer, alternating copolymer, periodic copolymer, block copolymer, radial copolymer, or graft copolymer), or a mixture thereof. As one of ordinary skill in the art will understand, the reactivity and functionality of a polymer may be altered by addition of a group such as, for example, amine, amide, carboxyl, hydroxyl, ester, ether, epoxide, anhydride, isocyanate, silane, ketone, and aldehyde. The dispersing polymeric material may comprise a polymer capable of crosslinking, entanglement, or hydrogen bonding in order to increase its toughness or its resistance to heat, moisture, or chemicals.

Exemplary dispersing polymeric materials include, by way of example and not by limitation, polyamides (e.g., Nylon 6, Nylon 6/6, Nylon 12, polyaspartic acid, polyglutamic acid, and so forth), polyamines, polyimides, polyacrylics (e.g., polyacrylamide, polyacrylonitrile, esters of methacrylic acid and acrylic acid, and so forth), polycarbonates (e.g., polybisphenol A carbonate, polypropylene carbonate, and so forth), polydienes (e.g., polybutadiene, polyisoprene, polynorbornene, and so forth), polyepoxides, polyesters (e.g., polyethylene terephthalate, polybutylene terephthalate, polytrimethylene terephthalate, polycaprolactone, polyglycolide, polylactide, polyhydroxybutyrate, polyhydroxyvalerate,

polyethylene adipate, polybutylene adipate, polypropylene succinate, and so forth), polyethers (e.g., polyethylene glycol (polyethylene oxide), polybutylene glycol, polypropylene oxide, polyoxymethylene (paraformaldehyde), polytetramethylene ether (polytetrahydrofuran), polyepichlorohydrin, and so forth), polyfluorocarbons, formaldehyde polymers (e.g., urea-formaldehyde, melamine-formaldehyde, phenol formaldehyde, and so forth), natural polymers (e.g., cellulose, chitosans, lignins, waxes, and so forth), polyolefins (e.g., polyethylene, polypropylene, polybutylene, polybutene, polyoctene, and so forth), polyphenylenes (e.g., polyphenylene oxide, polyphenylene sulfide, polyphenylene ether sulfone, and so forth), silicon containing polymers (e.g., polydimethyl siloxane, polycarbomethyl silane, and so forth), polyurethanes, polyvinyls (e.g., polyvinyl butyral, polyvinyl alcohol, polyvinyl acetate, polystyrene, polymethylstyrene, polyvinyl chloride, polyvinyl pyrrolidone, polymethyl vinyl ether, polyethyl vinyl ether, polyvinyl methyl ketone, and so forth), polyacetals, polyarylates, copolymers (e.g., polyethylene-co-vinyl acetate, polyethylene-co-acrylic acid, polybutylene terephthalate-co-polytetramethylene terephthalate, polylauryllactam-block-polytetrahydrofuran, and so forth), and mixtures thereof.

According to some embodiments of the invention, the polymeric composite typically comprises from about 10 percent to about 30 percent by weight of the dispersing polymeric material. And, according to one presently preferred embodiment, the polymeric composite may comprise 15 percent by weight of the dispersing polymeric material.

In general, the matrix polymeric material may comprise any polymer (or mixture of polymers) that has or provides one or more desired physical properties for the polymeric composite or an article (e.g., a synthetic fiber) made therefrom. Exemplary physical properties include, by way of example and not by limitation, mechanical properties (e.g., ductility, tensile strength, and hardness), thermal properties (e.g., thermoformability), and chemical properties (e.g., reactivity). According to some embodiments of the invention, the matrix polymeric material is compatible with or has an affinity for the dispersing polymeric material. Such affinity may facilitate forming a blend of the matrix polymeric material, the dispersing polymeric material, and the temperature regulating material during manufacture of the polymeric composite and, thus, ultimately facilitates incorporation of more uniform or greater amounts or loading level of a phase change material in the polymeric composite. As discussed previously, the dispersing polymeric material may serve as a compatibilizing link between the matrix polymeric material and the temperature

regulating material to thereby facilitate incorporating the temperature regulating material in the polymeric composite.

It should be recognized that the matrix polymeric material may be selected to be compatible with or have an affinity for the temperature regulating material. In
5 embodiments where the temperature regulating material further comprises a containment structure, the matrix polymeric material may be selected for its affinity for the containment structure in conjunction with, or as an alternative to, its affinity for a phase change material. According to some embodiments of the invention, the matrix polymeric material may have a slight or partial compatibility with or affinity for the temperature regulating material.
10 Such partial affinity may be adequate to facilitate dispersion of the temperature regulating material and to facilitate processing at higher temperatures. At lower temperatures and shear conditions and once the polymeric composite has been formed, this partial affinity may allow the temperature regulating material to separate out. For embodiments of the invention wherein a phase change material in a raw form is used, this partial affinity may
15 lead to insolubilization of the phase change material and increased phase change material domain formation within the polymeric composite.

Typically, the matrix polymeric material comprises a thermoplastic polymer (or mixture of thermoplastic polymers) (i.e., one that can be heated to form a melt and subsequently shaped or molded to form the polymeric composite). According to some
20 embodiments of the invention, the matrix polymeric material desirably comprises one or more high molecular weight polymers. A high molecular weight polymer typically has enhanced physical properties (e.g., mechanical properties) but may have a high viscosity when heated to form a melt. As one of ordinary skill in the art will understand, some polymers may be provided in a variety of forms having different molecular weights, since
25 the molecular weight of a polymer may be determined by conditions used for manufacturing the polymer. Accordingly, as used herein, the term "high molecular weight polymer" may refer to a high molecular weight form of a polymer (e.g., a high molecular weight form of an exemplary polymer discussed below). For instance, a polyester having a number average molecular weight of about 20,000 (or more) may be used as the high molecular weight
30 polymer in an embodiment of the invention. It should be recognized that a molecular weight or range of molecular weights associated with a high molecular weight polymer may depend on the particular polymer selected (e.g., polyester) or on the method or equipment used to mix the temperature regulating material with the high molecular weight polymer.

As with the dispersing polymeric material, the matrix polymeric material may comprise a polymer (or mixture of polymers) having a variety of chain structures that include one or more types of monomer units. In particular, the matrix polymeric material may comprise a linear polymer, a branched polymer (e.g., star branched polymer, comb
5 branched polymer, or dendritic branched polymer), or a mixture thereof. The matrix polymeric material may comprise a homopolymer, a copolymer (e.g., statistical copolymer, random copolymer, alternating copolymer, periodic copolymer, block copolymer, radial copolymer, or graft copolymer), or a mixture thereof. The reactivity and functionality of a polymer may be altered by addition of a group such as, for example, amine, amide,
10 carboxyl, hydroxyl, ester, ether, epoxide, anhydride, isocyanate, silane, ketone, and aldehyde, and the matrix polymeric material may comprise a polymer capable of crosslinking, entanglement, or hydrogen bonding in order to increase its toughness or its resistance to heat, moisture, or chemicals.

Exemplary matrix polymeric materials include, by way of example and not by
15 limitation, polyamides (e.g., Nylon 6, Nylon 6/6, Nylon 12, polyaspartic acid, polyglutamic acid, and so forth), polyamines, polyimides, polyacrylics (e.g., polyacrylamide, polyacrylonitrile, esters of methacrylic acid and acrylic acid, and so forth), polycarbonates (e.g., polybisphenol A carbonate, polypropylene carbonate, and so forth), polydienes (e.g., polybutadiene, polyisoprene, polynorbornene, and so forth), polyepoxides, polyesters (e.g.,
20 polyethylene terephthalate, polybutylene terephthalate, polytrimethylene terephthalate, polycaprolactone, polyglycolide, polylactide, polyhydroxybutyrate, polyhydroxyvalerate, polyethylene adipate, polybutylene adipate, polypropylene succinate, and so forth), polyethers (e.g., polyethylene glycol (polyethylene oxide), polybutylene glycol, polypropylene oxide, polyoxymethylene (paraformaldehyde), polytetramethylene ether
25 (polytetrahydrofuran), polyepichlorohydrin, and so forth), polyfluorocarbons, formaldehyde polymers (e.g., urea-formaldehyde, melamine-formaldehyde, phenol formaldehyde, and so forth), natural polymers (e.g., cellulose, chitosans, lignins, waxes, and so forth), polyolefins (e.g., polyethylene, polypropylene, polybutylene, polybutene, polyoctene, and so forth), polyphenylenes (e.g., polyphenylene oxide, polyphenylene sulfide, polyphenylene
30 ether sulfone, and so forth), silicon containing polymers (e.g., polydimethyl siloxane, polycarbomethyl silane, and so forth), polyurethanes, polyvinyls (e.g., polyvinyl butyral, polyvinyl alcohol, polyvinyl acetate, polystyrene, polymethylstyrene, polyvinyl chloride, polyvinyl pyrrolidone, polymethyl vinyl ether, polyethyl vinyl ether, polyvinyl methyl ketone, and so forth), polyacetals, polyarylates, copolymers (e.g., polyethylene-co-vinyl

acetate, polyethylene-co-acrylic acid, polybutylene terephthalate-co-polytetramethylene terephthalate, polylauryllactam-block-polytetrahydrofuran, and so forth), and mixtures thereof.

5 According to some embodiments of the invention, the polymeric composite typically comprises from about 40 percent to about 80 percent by weight of the matrix polymeric material. And, according to one presently preferred embodiment, the polymeric composite may comprise 70 percent by weight of the matrix polymeric material.

A general approach to forming a polymeric composite according to some
10 embodiments of the invention is discussed below. Initially, a temperature regulating material, a dispersing polymeric material, and a matrix polymeric material are provided. As discussed previously, the temperature regulating material may comprise a phase change material and may further comprise a containment structure (e.g., microcapsules) to encapsulate, contain, surround, or absorb the phase change material. According to some
15 embodiments of the invention, the dispersing polymeric material may comprise a low molecular weight polymer having an affinity for the containment structure or the phase change material, and the matrix polymeric material may comprise a high molecular weight polymer having an affinity for the dispersing polymeric material and providing one or more desired physical properties to the polymeric composite or to an article made therefrom.

Next, the temperature regulating material is mixed with the dispersing polymeric
20 material to form a first blend. According to some embodiments of the invention, the dispersing polymeric material is melted to form a first melt, and the temperature regulating material is dispersed in the first melt to form the first blend.

A second blend is then formed using the first blend and the matrix polymeric
25 material. According to some embodiments of the invention, the first blend is processed to form granules, and the granules are mixed with the matrix polymeric material to form the second blend. In particular, the matrix polymeric material may be melted to form a second melt, and the granules may be dispersed in the second melt to form the second blend. Alternatively, the second blend may be formed by melting the granules and adding the matrix polymeric material thereto. According to other embodiments of the invention,
30 granules need not be formed, and the first blend is mixed with the matrix polymeric material to form the second blend.

Once formed, the second blend is processed to form the polymeric composite.
According to some embodiments of the invention, the second blend is processed to form

pellets having enhanced reversible thermal properties provided by the phase change material incorporated therein.

The invention is more fully appreciated with reference to FIG. 1, which illustrates a manufacturing process for forming a polymeric composite in accordance with an embodiment of the invention.

With reference to FIG. 1, a temperature regulating material is provided (step 10). In the present embodiment, the temperature regulating material comprises a phase change material and a plurality of microcapsules that contain the phase change material. Here, the temperature regulating material may further comprise an amount of water wetting, coating, or absorbed by the microcapsules to form water-wetted microcapsules. These water-wetted microcapsules may form a wet cake. The wet cake may comprise from about 1 percent to about 90 percent by weight of the microcapsules and the phase change material with a remaining portion comprising water. Typically, the wet cake comprises from about 60 percent to about 70 percent by weight of the microcapsules and the phase change material with a remaining portion comprising water. According to some embodiments of the invention, use of this wet cake may serve to facilitate handling of the microcapsules or may improve dispersion (e.g., prevent lumping) of the microcapsules in a melt of the dispersing polymeric material.

As an alternative to or in conjunction with the microcapsules, other containment structures may be used to encapsulate, contain, surround, or absorb the phase change material. Also, it should be recognized that the temperature regulating material may, alternatively or in conjunction, comprise a phase change material in a raw form. The phase change material in the raw form may be provided as a solid in a variety of forms (e.g., bulk form, powders, pellets, granules, flakes, and so forth) or as a liquid in a variety of forms (e.g., molten form, dissolved in a solvent, and so forth).

Next, a dispersing polymeric material is provided (step 11). As discussed previously, the dispersing polymeric material may comprise any polymer (or mixture of polymers) that facilitates incorporating the temperature regulating material in the polymeric composite. In the present embodiment, the dispersing polymeric material comprises a low molecular weight polymer having an affinity for the microcapsules. It should be recognized that the dispersing polymeric material may comprise one or more additional polymers (e.g., one or more additional low molecular weight polymers).

As shown in FIG. 1, the temperature regulating material is mixed with the dispersing polymeric material to form a first blend (step 12). In accordance with the present

embodiment, the dispersing polymeric material is initially melted to form a first melt (e.g., in a heated mixing bowl or in a wet flushing apparatus), and the temperature regulating material (e.g., the wet cake) is added to and dispersed in the first melt to form a first blend. Uniform dispersion of the microcapsules containing the phase change material in the first melt may be facilitated by the affinity of the dispersing polymeric material for the microcapsules. Also, dispersion may be facilitated by maintaining the dispersing polymeric material in a molten state or by mixing (e.g., agitation or stirring). In the present embodiment, the water of the wet cake may be substantially removed by wet flushing. In particular, the first blend may be heated until the water of the wet cake is substantially eliminated such that, for example, the first blend comprises less than about 1 percent by weight of water. It should be recognized that step 12 may alternatively comprise dry blending the temperature regulating material with the dispersing polymeric material to form a dry blend, which may be subsequently heated to form the first blend.

Once formed, the first blend is processed to form granules (steps 14 and 15). In the present embodiment, the first blend is cooled to form a first solid (step 14), and the first solid is granulated to form the granules (step 15). According to some embodiments of the invention, the first blend is extruded, for example, into a thread (or threads), which thread is cooled and subsequently granulated to form the granules. Extrusion may be performed using any extruder (including any conventional extruder such as a single screw extruder) to form a thread having a variety of regular or irregular cross sectional shapes.

In general, any method (including any conventional method) may be used to granulate the first solid. For instance, the first solid may be pulverized, cut, or chopped using any conventional method to form the granules. The granules may be formed with a variety of shapes (e.g., spherical, ellipsoidal, cylindrical, powdered form, irregularly shaped, and so forth) and sizes. The granules may have the same or different shapes or sizes and may be formed with smooth or rough surfaces. According to some embodiments of the invention, the granules may have a maximum linear dimension (e.g., length or diameter) ranging from about 0.01 to about 10 millimeters and typically from about 1 to about 5 millimeters.

The granules may comprise from about 30 percent to about 60 percent by weight of the temperature regulating material (e.g., by dry weight of the microcapsules and the phase change material enclosed therein) with a remaining portion comprising the dispersing polymeric material. According to some embodiments of the invention, the granules typically comprise from about 45 percent to about 55 percent by weight of the

microcapsules and the phase change material with a remaining portion comprising the dispersing polymeric material. As discussed above, the granules may also comprise a small amount of water (e.g., less than about 1 percent by weight of water).

5 A matrix polymeric material is provided (step 18), and as discussed previously, the matrix polymeric material may comprise any polymer (or mixture of polymers) that provides one or more desired physical properties for the polymeric composite or for an article made therefrom. In the present embodiment, the matrix polymeric material comprises a high molecular weight polymer (or polymers) having an affinity for the dispersing polymeric material and providing desired physical properties such as, for
10 example, desired mechanical or thermal properties.

The granules formed from step 15 are mixed with the matrix polymeric material to form a second blend (step 17). In accordance with the present embodiment, the matrix polymeric material is initially melted to form a second melt, and the granules are added to and dispersed in the second melt to form a second blend. Dispersion of the granules in the
15 second melt may be facilitated by the affinity of the matrix polymeric material for the dispersing polymeric material. Moreover, the granules typically melt after being added to the second melt to release the microcapsules containing the phase change material, and uniform dispersion of the microcapsules in the second melt may be facilitated by the affinity of the matrix polymeric material for the dispersing polymeric material and the affinity of the
20 dispersing polymeric material for the microcapsules. Dispersion may also be facilitated by maintaining the matrix polymeric material in a molten state or by mixing (e.g., agitation or stirring). In the present embodiment, the water of the wet cake may be further removed by wet flushing. It should be recognized that step 17 may alternatively comprise dry blending the granules with the matrix polymeric material to form a dry blend, which may be
25 subsequently heated to form the second blend.

Once formed, the second blend is processed to form the polymeric composite (steps 20 and 21). As discussed previously, the polymeric composite may be formed in a variety of shapes, such as, by way of example and not by limitation, pellets, fibers, flakes, sheets, films, rods, and so forth. In the present embodiment, the second blend is cooled to form a
30 second solid (step 20), and the second solid is granulated to form pellets (step 21). According to some embodiments of the invention, the second blend is extruded, for example, into a thread (or threads), which thread is cooled and subsequently granulated to form the pellets. Extrusion may be performed using any extruder (including any

conventional extruder such as a single screw extruder) to form a thread having a variety of regular or irregular cross sectional shapes.

In general, any method (including any conventional method) may be used to granulate the second solid. For instance, the second solid may be pulverized, cut, or
5 chopped using any conventional method to form the pellets. The pellets may be formed with a variety of shapes (e.g., spherical, ellipsoidal, cylindrical, powdered form, irregularly shaped, and so forth) and sizes. The pellets may have the same or different shapes or sizes and may be formed with smooth or rough surfaces. According to some embodiments of the invention, the pellets may have a maximum linear dimension (e.g., length or diameter)
10 ranging from about 1 to about 10 millimeters and typically from about 1 to about 5 millimeters.

According to the present embodiment of the invention, the formed pellets typically comprise from about 10 percent to about 30 percent by weight of the temperature regulating material (e.g., the microcapsules and the phase change material), from about 10 percent to
15 about 30 percent by weight of the dispersing polymeric material, and from about 40 percent to about 80 percent by weight of the matrix polymeric material. In addition, the pellets may comprise an amount of water that is typically less than 1 percent by weight. The pellets may be used to form a variety of articles having enhanced reversible thermal properties such as, by way of example and not limitation, fibers such as synthetic fibers,
20 films, and injection molded articles.

FIG. 2 illustrates a manufacturing process to form a polymeric composite in accordance with another embodiment of the invention. As with the previous embodiment, a temperature regulating material, a dispersing polymeric material, and a matrix polymeric material are provided (steps 30-32).

As shown in FIG. 2, the temperature regulating material, the dispersing polymeric material, and the matrix polymeric material are then mixed together (step 33). In accordance with the present embodiment, the dispersing polymeric material is initially melted to form a first melt, and the temperature regulating material is added to and dispersed in the first melt to form a first blend. If present, water may be substantially
25 removed by wet flushing. It should be recognized that the temperature regulating material may alternatively be dry blended with the dispersing polymeric material to form a dry blend, which may be subsequently heated to form the first blend. Next, the first blend is mixed with the matrix polymeric material to form a second blend. The matrix polymeric material may be initially melted to form a second melt, and the first blend may be mixed
30

with the second melt to form a second blend. Alternatively, the matrix polymeric material may be added to and dispersed in the first blend to form the second blend.

It should be recognized that the temperature regulating material, the dispersing polymeric material, and the matrix polymeric material may be mixed together using a variety of other methods to form the second blend. For instance, a polymeric blend of the dispersing polymeric material and the matrix polymeric material may be formed, and the temperature regulating material may be subsequently added to and dispersed in the polymeric blend to form the second blend. As another example, the temperature regulating material, the dispersing polymeric material, and the matrix polymeric material may be dry blended to form a dry blend, which may be subsequently heated to form the second blend. As a further example, the temperature regulating material, the dispersing polymeric material, and the matrix polymeric material may be provided together, heated, and mixed to form the second blend. In particular, the temperature regulating material, the dispersing polymeric material, and the matrix polymeric material may be fed into an extruder to form the second blend, according to some embodiments of the invention.

Once formed, the second blend is processed to form the polymeric composite (steps 35 and 36). As discussed previously, the polymeric composite may be formed in a variety of shapes, such as, by way of example and not by limitation, pellets, fibers, flakes, sheets, films, rods, and so forth. In the present embodiment, the second blend is cooled to form a solid (step 35), and the solid is granulated to form pellets (step 36). According to some embodiments of the invention, the second blend is extruded, for example, into a thread (or threads), which thread is cooled and subsequently granulated to form the pellets.

Turning next to FIG. 3, a manufacturing process to form a polymeric composite in accordance with a further embodiment of the invention is illustrated. In the present embodiment, the polymeric composite is formed using a multistage extruder 43. While the spirit and scope of this invention is not to be limited to the following definition, a multistage extruder is typically understood to comprise two or more extruder units that may be operatively connected in a variety of configurations (e.g., in series), wherein each extruder unit may be a single or multiple screw extruder, may have one or more inlet openings to receive a substance to be extruded, and one or more discharge ports to vent gases such as air, water (e.g., steam), and volatile materials.

As shown in FIG. 3, a temperature regulating material and a dispersing polymeric material are provided (steps 40 and 41) and are fed into the multistage extruder 43. The temperature regulating material and the dispersing polymeric material may be fed into the

same or different inlet openings of the multistage extruder 43. Within the multistage extruder 43, the temperature regulating material is mixed with the dispersing polymeric material to form a first blend, and the first blend is advanced through the multistage extruder 43 along a melt stream path 44.

5 Next, a matrix polymeric material is provided (step 42) and is fed into the multistage extruder 43. In the present embodiment, the matrix polymeric material is fed into an inlet opening downstream along the melt stream path 44. Alternatively, the matrix polymeric material may be fed into an inlet opening upstream along the melt stream path 44 (e.g., the same inlet opening used to receive the temperature regulating material or the dispersing
10 polymeric material). Within the multistage extruder 43, the first blend is mixed with the matrix polymeric material to form a second blend. As shown in FIG. 3, water, if present, may be removed through a discharge port (step 45).

 Once formed, the second blend is processed to form the polymeric composite (step 46). As discussed previously, the polymeric composite may be formed in a variety of
15 shapes, such as, by way of example and not by limitation, pellets, fibers, flakes, sheets, films, rods, and so forth. For example, the second blend may be extruded through a die into a thread (or threads), which thread is cooled and subsequently granulated to form pellets. As another example, the second blend may be extruded through a spinneret to form synthetic fibers.

20 As discussed previously, polymeric composites in accordance with some embodiments of the invention may be formed using one or more phase change materials in a raw form. For example, the manufacturing processes discussed above in connection with FIG. 1, FIG. 2, and FIG. 3 may employ a temperature regulating material that, alternatively or in conjunction, comprises a phase change material in a raw form. The phase change
25 material in the raw form may be provided as a solid in a variety of forms (e.g., bulk form, powders, pellets, granules, flakes, and so forth) or as a liquid in a variety of forms (e.g., molten form, dissolved in a solvent, and so forth) (e.g., at step 10 of FIG. 1, at step 30 of FIG. 2, or at step 40 of FIG. 3). For some embodiments of the invention, the phase change material in the raw form is incorporated into a polymeric composite, wherein the phase
30 change material may be contained within a plurality of isolated volumes or spaces that are dispersed throughout the polymeric composite.

 According to some embodiments of the invention, a phase change material in a raw form may be introduced at virtually any time during a manufacturing process to form a polymeric composite (e.g., at virtually any of the steps illustrated in FIG. 1, FIG. 2, and

FIG. 3). For instance, the phase change material may be introduced via liquid injection or by feeding the phase change material in a solid form alone or in conjunction with a dispersing polymeric material or a matrix polymeric material. A phase change material in a raw liquid form can be filtered or mixed to insure homogeneity prior to liquid injection. A phase change material in a raw solid form may be fed into a feed throat of an extruder or may be side stuffed into the extruder in order to prevent feed throat plugging. According to some embodiments of the invention, the phase change material in the raw form is desirably introduced at a later time during a manufacturing process to thereby ensure adequate dispersion of the phase change material or to reduce its exposure to manufacturing conditions (e.g., high temperature or shear forces) associated with forming the polymeric composite. By using such a late-stage addition of the phase change material, exposure of the phase change material to elevated temperatures and any subsequent degradation or loss of the phase change material may be reduced.

Various other embodiments are within the spirit and scope of the invention. For instance, a polymeric composite in accordance with some embodiments of the invention may comprise a temperature regulating material and either a dispersing polymeric material or a matrix polymeric material. Either the dispersing or matrix polymeric material may be selected to have an affinity for (or a slight or partial affinity for) the temperature regulating material. According to an embodiment of the invention, the polymeric composite may comprise a temperature regulating material and a matrix polymeric material that desirably comprises one or more high molecular weight polymers. In forming the polymeric composite, the temperature regulating material and either the dispersing or matrix polymeric material may be mixed to form a blend, and the blend may then be processed to form the polymeric composite.

As discussed previously, polymeric composites in accordance with the invention may be further processed to form a variety of articles having enhanced reversible thermal properties. For instance, pellets formed in accordance with some embodiments of the invention may be used to form synthetic fibers, for injection molding processes, or for extrusion processes. In particular, the pellets may be used in a melt spinning process to form synthetic fibers comprising, for example, from about 10 percent to about 30 percent by weight of a temperature regulating material. Once formed, the synthetic fibers may be collected into a strand or made into a cut staple. The synthetic fibers can be used to make woven or non-woven fabric materials, or alternatively, the synthetic fibers can be wound into a yarn to be used thereafter in a weaving or a knitting process to form a synthetic fabric

material. It should be recognized that the pellets may be mixed with one or more polymers (e.g., one or more thermoplastic polymers) to form a blend, which one or more polymers may be the same as or different from polymer(s) comprising the pellets. The resulting blend may then be processed to form synthetic fibers comprising, for example, from about 5 percent to about 10 percent by weight of the temperature regulating material. In addition, one or more thermoplastic polymers may be used in conjunction with the pellets to form multi-component melt spun fibers (e.g., bi-component fibers), multi-component extruded films, multi-component injection molded products, and so forth.

10

EXAMPLES

The following examples describe specific aspects of the invention to illustrate and provide a description of the invention for those of ordinary skill in the art. The examples should not be construed as limiting the invention, as the examples merely provide specific methodology useful in understanding and practicing the invention.

15

Example 1

About 5.0 pounds of a low molecular weight polyethylene homopolymer (AC-16 polyethylene, drop point of 102°C, manufactured by Honeywell Specialty Chemical) was added to a wet flushing apparatus, and the homopolymer was then slowly melted and mixed at about 110°C to about 130°C. Once the homopolymer was melted, about 8.47 pounds of a wet cake was slowly added to the molten homopolymer over about a 30 minute time period to form a first blend. The wet cake comprised water-wetted microcapsules containing a phase change material (micro PCM lot# M 42-31, 59.0 percent by weight of microcapsules and phase change material, manufactured by MicroTek Laboratories, Inc.).

25

Water was flashed off as the microcapsules containing the phase change material was added to and dispersed in the molten homopolymer. Mixing continued until less than about 0.15 percent by weight of the water remained (as measured using Karl-Fischer titration). The resulting first blend was then cooled to form a first solid, and the first solid was chopped to form a chopped material for further processing. The chopped material comprised about 50 percent by weight of the microcapsules and the phase change material.

30

A dry blend was then formed by dry blending about 30 pounds of the chopped material with about 70 pounds of a high molecular weight fiber-grade polypropylene thermoplastic polymer (Polypropylene homopolymer 6852 from PB Amoco Polymers).

The resulting dry blend was then extruded using a 2 ½ inch single screw extruder with all zones set at about 230°C, with a screw speed of about 70 rpm, with 150 mesh screens, and with a nitrogen purge, thus producing pellets. The pellets were then oven dried overnight at about 50°C and at about 1 mm Hg of vacuum.

5 The pellets, comprising about 15 percent by weight of microcapsules and the phase change material, were then extruded/melt spun at temperatures between about 230°C and 265°C and preferably at about 235°C to 245°C.

 Synthetic fibers were spun/wound at takeup speeds of up to about 1600 meters per minute (mpm) to yield from about 20 to about 6 deniers per fiber, and the synthetic fibers
10 exhibited enhanced reversible thermal properties provided by the phase change material as discussed in Example 2.

Example 2

 Differential Scanning Calorimeter (DSC) measurements of the above synthetic fibers were made using a Perkin Elmer Pyris 1 instrument. Cooling was accomplished
15 using a FTS Systems Intercoler 1. Data analysis was performed using a Perkin Elmer Pyris Thermal Analysis System and Software for Windows, version 3.72.

 Test samples were prepared in Perkin Elmer hermetically sealed aluminum sample pans, and testing was performed while the test samples were continuously subjected to N₂ flow.

20 Test conditions comprised: 1) cooling the test samples to about -10°C; 2) isothermal hold for about 1 minute at -10°C; 3) heating from -10°C to about 50°C at a rate of about 5°C per minute; 4) isothermal hold for about 1 minute at 50°C; and then 5) cooling from 50°C to about -10°C at a rate of about 5°C per minute.

 Using the DSC measurements as described above, the synthetic fibers provided
25 between about 17.5 and 23.2 J/g of thermal energy storage capacity.

Example 3

 About 3.1307 grams of a phase change material in a raw form (Kenwax 19 paraffin, blend of C18 through C24 paraffinic hydrocarbons, 150 J/g latent heat) was placed in a vial, and about 3.1255 grams of a polymeric material (Elvax 450, 18 percent by weight of vinyl
30 acetate, polyethylene-co-vinyl acetate polymer supplied by DuPont Inc.) having a slight or partial affinity for the phase change material was added to the vial. The phase change material and the polymeric material were mixed together at between 120°C to 130°C by hand to produce a 50:50 by weight blend that was homogeneous and clear. Upon cooling, a polymeric composite was formed, which polymeric composite was hazy and rubbery and

without a waxy or greasy feel. A DSC measurement of the polymeric composite showed 73.3 J/g of thermal energy storage capacity, which corresponds to 48.9 percent of the Kenwax 19 available to provide a thermal regulating property.

5 Each of the patent applications, patents, publications, and other published documents mentioned or referred to in this specification is herein incorporated by reference in its entirety, to the same extent as if each individual patent application, patent, publication, and other published document was specifically and individually indicated to be incorporated by reference.

10 While the present invention has been described with reference to the specific embodiments thereof, it should be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the true spirit and scope of the invention, as defined by the appended claims. In addition, many modifications may be made to adapt a particular situation, material, composition of matter,
15 method, process step or steps, to the objective, spirit and scope of the present invention. All such modifications are intended to be within the scope of the claims appended hereto. In particular, while the methods disclosed herein have been described with reference to particular steps performed in a particular order, it will be understood that these steps may be combined, sub-divided, or re-ordered to form an equivalent method without departing from
20 the teachings of the present invention. Accordingly, unless specifically indicated herein, the order and grouping of the steps is not a limitation of the present invention.

What is claimed is:

1. A method of manufacturing a polymeric composite, comprising:
 - (a) mixing a temperature regulating material with a dispersing polymeric material to form a first blend;
 - (b) processing the first blend to form granules;
 - (c) mixing the granules with a matrix polymeric material to form a second blend;
 - and
 - (d) processing the second blend to form the polymeric composite.
2. The method of claim 1, wherein the temperature regulating material comprises a phase change material that is selected from the group consisting of hydrocarbons, hydrated salts, waxes, oils, water, fatty acids, fatty acid esters, dibasic acids, dibasic esters, 1-halides, primary alcohols, aromatic compounds, clathrates, semi-clathrates, gas clathrates, stearic anhydride, ethylene carbonate, polyhydric alcohols, polymers, metals, and mixtures thereof.
3. The method of claim 1, wherein the temperature regulating material comprises a plurality of microcapsules containing a phase change material.
4. The method of claim 3, wherein the microcapsules are coated with water to form a wet cake.
5. The method of claim 4, further comprising heating the first blend until the first blend comprises less than about 1 percent by weight of water.
6. The method of claim 1, wherein the temperature regulating material comprises silica particles, zeolite particles, carbon particles, or an absorbent material impregnated with a phase change material.
7. The method of claim 1, wherein the dispersing polymeric material comprises a low molecular weight polymer.
8. The method of claim 1, wherein mixing the temperature regulating material with the dispersing polymeric material in (a) comprises:
 - melting the dispersing polymeric material to form a melt; and
 - dispersing the temperature regulating material in the melt to form the first blend.

9. The method of claim 8, wherein the temperature regulating material comprises a plurality of microcapsules containing a phase change material, and wherein the dispersing polymeric material has an affinity for the microcapsules to facilitate dispersing the microcapsules in the melt.
- 5 10. The method of claim 1, wherein processing the first blend to form the granules in (b) comprises:
cooling the first blend to form a solid; and
granulating the solid to form the granules.
- 10 11. The method of claim 1, wherein the matrix polymeric material comprises a high molecular weight polymer.
12. The method of claim 1, wherein mixing the granules with the matrix polymeric material in (c) comprises:
melting the matrix polymeric material to form a melt; and
dispersing the granules in the melt to form the second blend.
- 15 13. The method of claim 12, wherein the matrix polymeric material has an affinity for the dispersing polymeric material to facilitate dispersing the granules in the melt.
14. The method of claim 1, wherein mixing the granules with the matrix polymeric material in (c) comprises:
dry blending the granules with the matrix polymeric material to form a dry blend;
20 heating the dry blend to form the second blend.
15. The method of claim 1, wherein the polymeric composite is formed as pellets, fibers, flakes, a sheet, a film, or a rod.
16. The method of claim 1, wherein the polymeric composite is formed as pellets, and wherein processing the second blend in (d) comprises:
25 cooling the second blend to form a solid; and
granulating the solid to form the pellets.
17. The method of claim 1, wherein the polymeric composite comprises from about 10 percent to about 30 percent by weight of the temperature regulating material.

18. A method of manufacturing a polymeric composite useful to produce an article having enhanced reversible thermal properties, comprising:
- (a) melting a dispersing polymeric material to form a first melt;
 - (b) dispersing a temperature regulating material in the first melt to form a first blend,
 - 5 wherein the temperature regulating material comprises a phase change material;
 - (c) processing the first blend to form granules;
 - (d) melting a matrix polymeric material to form a second melt;
 - (e) dispersing the granules in the second melt to form a second blend; and
 - (f) processing the second blend to form the polymeric composite.
- 10 19. The method of claim 18, wherein the dispersing polymeric material is selected from the group consisting of polyethylene, polypropylene, Nylon 12, polybutylene terephthalate, polyethylene-co-vinyl acetate, polyethylene-co-acrylic acid, polybutylene terephthalate-co-polytetramethylene terephthalate, polylauryllactam-block-polytetrahydrofuran, and mixtures thereof.
- 15 20. The method of claim 18, wherein the phase change material is a hydrocarbon or a mixture of hydrocarbons.
21. The method of claim 18, wherein the temperature regulating material further comprises a plurality of microcapsules that contain the phase change material.
22. The method of claim 21, wherein the dispersing polymeric material comprises a low
20 molecular weight polymer having an affinity for the microcapsules.
23. The method of claim 18, wherein processing the first blend to form the granules in (c) comprises:
- extruding the first blend into a thread; and
 - granulating the thread to form the granules.
- 25 24. The method of claim 18, wherein the granules comprise from about 45 percent to about 55 percent by weight of the temperature regulating material.
25. The method of claim 18, wherein the matrix polymeric material comprises a high molecular weight polymer having an affinity for the dispersing polymeric material and providing desired physical properties for the article.

26. The method of claim 18, wherein the matrix polymeric material is selected from the group consisting of polyamides, polyamines, polyimides, polyacrylics, polycarbonates, polydienes, polyepoxides, polyesters, polyethers, polyflourocarbons, formaldehyde polymers, natural polymers, polyolefins, polyphenylenes, silicon containing polymers, polyurethanes, polyvinyls, polyacetals, polyarylates, and mixtures thereof.
27. The method of claim 18, wherein the polymeric composite is formed as pellets, and wherein processing the second blend in (f) comprises:
extruding the second blend into a thread; and
granulating the thread to form the pellets.
28. The method of claim 27, wherein the pellets comprise from about 10 percent to about 30 percent by weight of the temperature regulating material.
29. The method of claim 27, wherein the pellets comprise from about 15 percent to about 25 percent by weight of the temperature regulating material.
30. A method of manufacturing a polymeric composite, comprising:
(a) melting a dispersing polymeric material to form a first melt;
(b) dispersing a temperature regulating material in the first melt to form a first blend, wherein the temperature regulating material comprises a phase change material;
(c) mixing the first blend with a matrix polymeric material to form a second blend;
and
(d) processing the second blend to form the polymeric composite.
31. The method of claim 30, wherein the dispersing polymeric material comprises a low molecular weight polymer having an affinity for the phase change material.
32. The method of claim 30, wherein the temperature regulating material further comprises a containment structure that contains the phase change material, and wherein the containment structure comprises microcapsules, silica particles, zeolite particles, carbon particles, or an absorbent material.
33. The method of claim 30, wherein the dispersing polymeric material and the matrix polymeric material are different.

34. The method of claim 30, wherein the matrix polymeric material comprises a high molecular weight polymer having an affinity for the dispersing polymeric material.
35. The method of claim 30, wherein the matrix polymeric material comprises a thermoplastic polymer or a mixture of thermoplastic polymers.
- 5 36. The method of claim 30, wherein mixing the first blend with the matrix polymeric material in (c) comprises:
- melting the matrix polymeric material to form a second melt; and
 - mixing the first blend with the second melt to form the second blend.
- 10 37. The method of claim 30, wherein the polymeric composite is formed as pellets, fibers, flakes, a sheet, a film, or a rod.
38. The method of claim 30, wherein the polymeric composite is formed as pellets, and wherein processing the second blend in (d) comprises extruding the second blend to form the pellets.

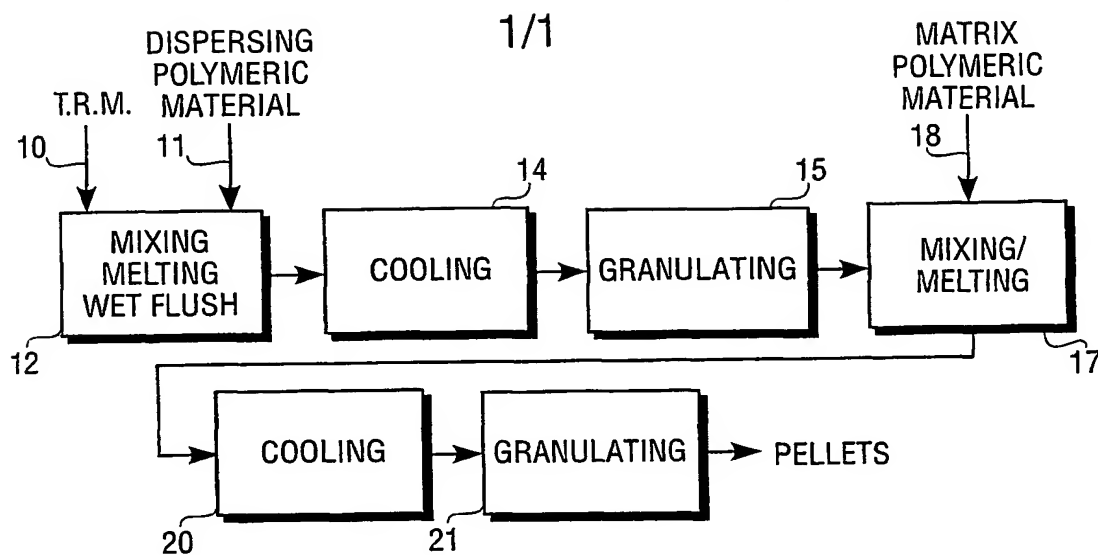


FIG. 1

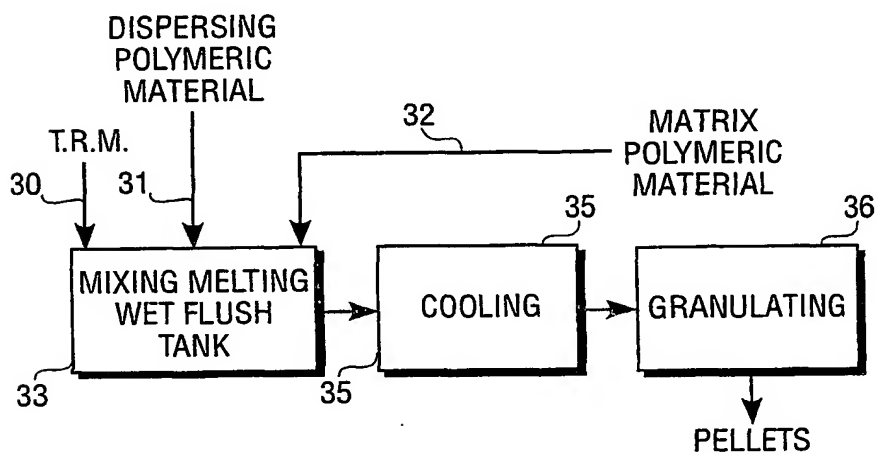


FIG. 2

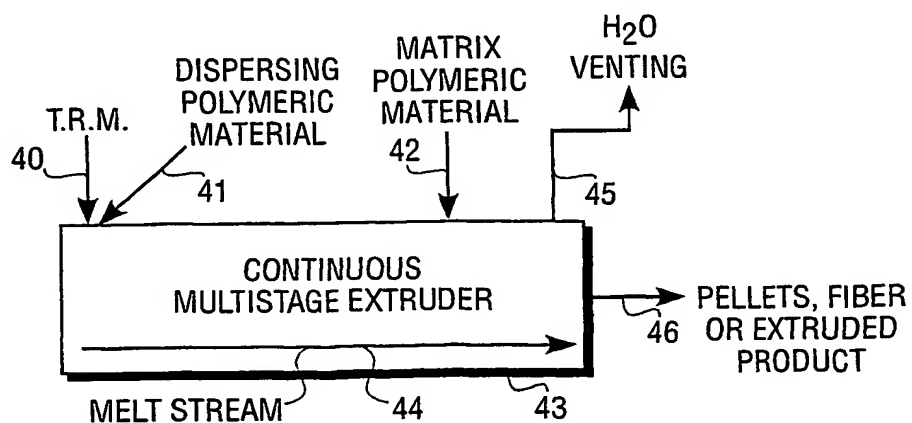


FIG. 3

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
28 March 2002 (28.03.2002)

PCT

(10) International Publication Number
WO 02/24789 A3

(51) International Patent Classification⁷: C08J 3/22.
D01F 1/02

(21) International Application Number: PCT/US01/29724

(22) International Filing Date:
21 September 2001 (21.09.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/234,150 21 September 2000 (21.09.2000) US
09/777,512 6 February 2001 (06.02.2001) US

(71) Applicant: OUTLAST TECHNOLOGIES, INC.
[US/US]; 6235 Lookout Road, Boulder, CO 80301 (US).

(72) Inventors: MAGILL, Monte, C.: 449 Westview Court,
Longmont, CO 80501 (US). HARTMANN, Mark, H.:
256 Rockview Drive, Superior, CO 80027 (US).

(74) Agents: GALLIANI, William, S.: Cooley Godward LLP,
3000 El Camino Real, Five Palo Alto Square, Palo Alto,
CA 94306-2155 et al. (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI,
SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA,
ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,
TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

(88) Date of publication of the international search report:
30 May 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: POLYMERIC COMPOSITES HAVING ENHANCED REVERSIBLE THERMAL PROPERTIES AND METHODS OF MANUFACTURING THEREOF

(57) Abstract: A polymeric composite having enhanced reversible thermal properties is manufactured. A temperature regulating material is mixed with a dispersing polymeric material to form a first blend. The first blend is processed to form granules, and the granules are mixed with a matrix polymeric material to form a second blend. The second blend is processed to form the polymeric composite. The polymeric composite may be formed in a variety of shapes, such as, for example, pellets, fibers, flakes, sheets, films, rods, and so forth. The polymeric composite may be used as is or incorporated in various articles and applications where a thermal regulating property is desired. The polymeric composite may be further processed to form a variety of articles having enhanced reversible thermal properties, such as, for example, melt spun synthetic fibers.

WO 02/24789 A3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/29724

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J3/22 D01F1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 088 370 A (UNION CARBIDE AUSTRALIA) 14 September 1983 (1983-09-14) claims 1-12 page 8, line 14 - line 26 page 9, line 14 - page 10, line 6 example 1	1,2,14, 15
X	US 5 366 645 A (SOBOTKA RICHARD) 22 November 1994 (1994-11-22) claims 1,3,8,9 examples 1,5	1,2,6,8, 12-15, 18,19, 23,26,30
X	US 4 617 332 A (GRIFFEN CHARLES W ET AL) 14 October 1986 (1986-10-14) claims 1,2 column 3, line 35 - line 59 -/--	1,2

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

5 April 2002

Date of mailing of the international search report

15/04/2002

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Hallemeesch, A

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/29724

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 756 958 A (BRYANT YVONNE G ET AL) 12 July 1988 (1988-07-12) claims 1,4 column 3, line 23 - line 64 ---	1,3
A	US 5 851 338 A (PUSHAW ROBERT J) 22 December 1998 (1998-12-22) ---	
A	US 4 851 291 A (VIGO TYRONE L ET AL) 25 July 1989 (1989-07-25) -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/29724

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0088370	A	14-09-1983	AU 1182883 A EP 0088370 A2 JP 58193120 A NZ 203447 A	08-09-1983 14-09-1983 10-11-1983 11-10-1985
US 5366645	A	22-11-1994	DE 4116396 A1 AU 649815 B2 AU 1607392 A CA 2068604 A1 CN 1066861 A EP 0524386 A2 FI 922239 A JP 5178607 A ZA 9203418 A	19-11-1992 02-06-1994 19-11-1992 19-11-1992 09-12-1992 27-01-1993 19-11-1992 20-07-1993 27-01-1993
US 4617332	A	14-10-1986	IN 168320 A1 US 4797160 A US RE34880 E	09-03-1991 10-01-1989 21-03-1995
US 4756958	A	12-07-1988	CA 1315083 A1 DE 3854106 D1 DE 3854106 T2 EP 0306202 A2 JP 1085374 A JP 1851056 C JP 5055607 B	30-03-1993 10-08-1995 08-02-1996 08-03-1989 30-03-1989 21-06-1994 17-08-1993
US 5851338	A	22-12-1998	JP 3244451 B2 JP 10305507 A US 5677048 A WO 9846669 A1 US 5955188 A EP 0981576 A1 DE 981576 T1	07-01-2002 17-11-1998 14-10-1997 22-10-1998 21-09-1999 01-03-2000 14-09-2000
US 4851291	A	25-07-1989	AT 142127 T AU 603124 B2 AU 7690587 A DE 3751894 D1 DE 3751894 T2 DK 85588 A EP 0311642 A1 FI 885864 A JP 1503632 T JP 2661931 B2 KR 9403137 B1 NO 880722 A ,B, WO 8707854 A1 US 4908238 A	15-09-1996 08-11-1990 12-01-1988 10-10-1996 06-02-1997 18-02-1988 19-04-1989 19-12-1988 07-12-1989 08-10-1997 15-04-1994 18-04-1988 30-12-1987 13-03-1990